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# <Division of Synthetic Chemistry>Structural Organic Chemistry

AUTHOR(S):

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# Division of Synthetic Chemistry – Structural Organic Chemistry –

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Prof  
MURATA, Yasujiro  
(D Eng)



Assoc Prof  
HIROSE, Takashi  
(D Eng)



Assist Prof  
HASHIKAWA, Yoshifumi  
(D Eng)



Program-Specific Res  
IDE, Yuki  
(D Sc)



Program-Specific Res  
KIZAKI, Kazuro  
(D Eng)



## Researcher (pt)

ADACHI, Ayumi

## Students

PD  
ZHANG, Sheng  
(Ph D)

HUANG, Guanglin (D1)  
OKAMOTO, Shu (M2)  
KANAYA, Taku (M1)

LI, Hui (M1)  
LI, Jiayue (RS)  
ZENG, Yuting (RS)

ZHU, Xiaotan (RS)  
KOYAMA, Tomohisa (UG)  
TANIGUCHI, Junichiro (UG)

## Scope of Research

Fundamental studies are being conducted for the creation of new functional  $\pi$ -systems with novel structures and properties, and for evaluation of their application as organic semiconducting materials for photovoltaic and electroluminescent devices. The major subjects are: 1) organochemical transformation of fullerenes  $C_{60}$  and  $C_{70}$ , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; 2) generation of ionic fullerene species and their application for the synthesis of functional material; 3) synthesis of new carbon-rich materials by the use of transition metal complex; and 4) creation of new functional  $\pi$ -materials with unique photoelectric properties.

### KEYWORDS

$\pi$ -Conjugated Systems      Endohedral Fullerenes  
Functional Materials      Helical Structures  
Radical Species

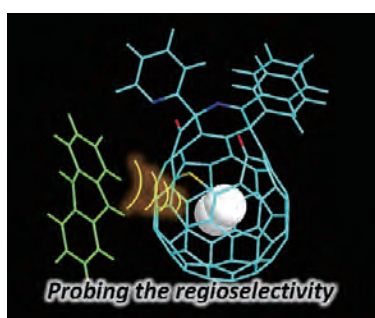


## Selected Publications

Hashikawa, Y.; Murata, Y., Probing the Regioselectivity Using an Entrapped  $H_2$ : Diels-Alder Reaction of a Cage Opened  $C_{60}$  Derivative with Anthracene, *Chem. Eur. J.*, **25**, 2482-2485 (2019).  
Suzuki, H.; Nakano, M.; Hashikawa, Y.; Murata, Y., Rotational Motion and Nuclear Spin Interconversion of  $H_2O$  Encapsulated in  $C_{60}$  Appearing in the Low-Temperature Heat Capacity, *J. Phys. Chem. Lett.*, **10**, 1306-1311 (2019).  
Fujii, S.; Cho, H.; Hashikawa, Y.; Nishino, T.; Murata, Y.; Kiguchi, M., Tuneable Single-Molecule Electronic Conductance of  $C_{60}$  by Encapsulation, *Phys. Chem. Chem. Phys.*, **21**, 12606-12610 (2019).  
Hashikawa, Y.; Murata, Y.,  $H_2O$ /Olefinic- $\pi$  Interaction inside a Carbon Nanocage, *J. Am. Chem. Soc.*, **141**, 12928-12938 (2019).  
Adachi, K.; Hirose, T.; Matsuda, K., Polymorphism of Porphyrin 2D Assemblies at the Liquid-Graphite Interface: Effect of Polar Solvent Additive and Flexible Spacer on the Face-On and Edge-On Type Molecular Arrangements, *Chem. Commun.*, **55**, 8836-8839 (2019).

## Probing the Regioselectivity Using an Entrapped $H_2$ : Diels-Alder Reaction of a Cage Opened $C_{60}$ Derivative with Anthracene

We have studied the regioselectivity in the Diels-Alder reaction of an open-cage  $C_{60}$  derivative with anthracene (Figure 1). By using an encapsulated  $H_2$  molecule as a magnetic probe, we successfully evaluated the product population in detail, indicating the formation of ca. 10 compounds as major components. The NICS calculations showed the close resemblance to the observed  $^1H$  NMR spectrum, which realizes facile characterization of the products. We further performed theoretical studies for forming all 29 possible anthracene-adducts. The results indicated that the regioselectivity is strongly governed by steric factor, frontier orbital coefficients, and thermodynamic stabilities. The single crystal X-ray analysis of the most dominant compound exhibited the supramolecular architecture between the anthracene moiety and the  $\pi$ -sphere of a neighbouring molecule.

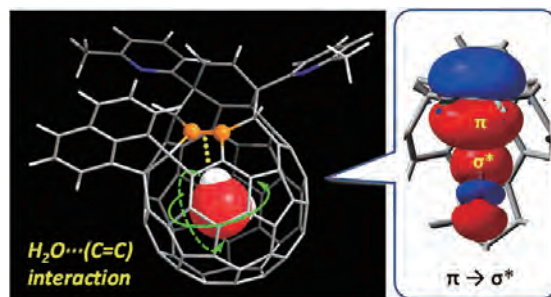


**Figure 1.** Regioselectivity on the Diels-Alder reaction of an open-cage  $C_{60}$  derivative with anthracene, probed by an encapsulated  $H_2$  molecule.

## $H_2O/Olefinic-\pi$ Interaction inside a Carbon Nanocage

The  $H_2O/CH_2=CH_2$ -type hydrogen-bonding (H-bonding) model was experimentally constructed using a water complex of an open-cage  $C_{60}$  derivative, in which an olefinic double bond and a single molecule of  $H_2O$  are geometrically confined (Figure 2). To investigate  $OH/\pi$ -type H-bonding, that is,  $H_2O \cdots (C=C)$  interaction, we performed  $^1H$  NMR spectroscopic studies that demonstrated the monotonic downfield shift of the proton signal corresponding to  $H_2O$  with remarkable rotational perturbation by lowering the temperature. From the temperature dependence of the angular momentum correlation time ( $\tau_1$ ), the interaction energy was quantitatively estimated to be ca. 0.3 kcal/mol. Based on comprehensive computational studies, the orientation of  $H_2O$  was found to play a prominent role to vary the bonding strength as well as contribution from the

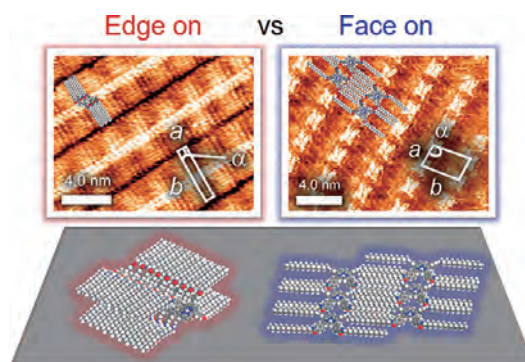
electrostatic attraction and orbital-orbital interaction significantly driven by the favorable orbital overlap identified as  $\pi(C=C) \rightarrow \sigma^*(OH)$  interaction.



**Figure 2.** The experimental model of a water-olefin complex based on an open-cage  $C_{60}$  derivative encapsulating a water molecule.

## Polymorphism of Porphyrin 2D Assemblies at the Liquid–Graphite Interface: Effect of Polar Solvent Additive and Flexible Spacer on the Face-On and Edge-On Type Molecular Arrangements

Precise control over the intermolecular arrangement in ordered assemblies is of primary importance for the development of functional materials in the solid state. In the case where multiple crystal structures are obtained, i.e., so-called polymorphism is observed, selecting a specific molecular arrangement is a straightforward approach to control the solid state properties. In this study, we found that the molecular orientation of porphyrin two-dimensional assemblies at solid-liquid interfaces can be controlled by using intermolecular hydrogen bonds of amide groups (Figure 3). When phenyloctane was used as the solution phase, intermolecular hydrogen bonds were effectively formed and an edge-on orientation was selectively observed. On the other hand, only face-on orientation was observed when octanoic acid was used. Interestingly, the addition of only 0.5 vol% of a polar solvent was found to significantly affect the selectivity of molecular orientation.



**Figure 3.** The two-dimensional polymorphs of porphyrin assembly at the liquid/solid interface.